ADSORPTION OF CD(II), NI(II) AND CU(II) USING ACTIVATED ROCK MELON SHELL WASTE : KINETICS AND EQUILIBRIUM

AMALINA BINTI ROSLAN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2014

ABSTRACT

Heavy metals in wastewater exhibit a global concern of environment due to its toxicity characteristics to many organisms. Adsorption can be used for high separation efficiency of heavy metals in waste water. This method widely used in this industry using different type of adsorbent. The use of low-cost adsorbents has been investigated as a replacement for current costly methods of removing heavy metals from solution. The objective of this research is to investigate the potential of rock melon shell waste as alternative adsorbent to adsorb Cd (II), Ni (II) and Cu (II) ions on aqueous solution. In this research, rock melon shell is used to replace the highly cost adsorbent used in the waste water industry The rock melon shell will be dried, ground and separate by their size through sieve shaker. Then, the rock melon shell powder was activated in the furnace at temperature range 400 ˚C - 650 ˚C. The prepared adsorbent and adsorbate were used for testing the removal effect of the heavy metals by manipulating the parameters of solution pH, contact time and adsorbent dosage. The results were analyzed by using the Atomic Absorption Spectroscopy (AAS). The optimal process conditions were used for kinetic and adsorption equilibrium. The percentage removal of Cd (II), Ni (II) and Cu (II) had been measured and modeled. The percent adsorption of Cd (II), Ni (II) and Cu (II) increased with increased in pH, contact time and adsorbent dosage. However, it tends to achieve equilibrium state once the active sites of the adsorbent are fully occupied. The condition where it gave the highest percentage removal is at 120 minutes contact time, at pH=8 and adsorbent dosage of 0.3g which is exceed 99%. Adsorption of Cd (II), Ni (II) and Cu (II) ions from aqueous solution approved the second-order kinetic yielding good R^2 values of 1.00 and k values of 0.0781 to 0.1776.

ABSTRAK

Logam berat dalam air sisa mempamerkan satu kebimbangan global alam sekitar kerana ciri-ciri ketoksikan kepada kebanyakan organisma. Penjerapan boleh digunakan untuk kecekapan pemisahan logam berat yang tinggi dalam air sisa. Kaedah ini digunakan secara meluas dalam industri menggunakan jenis bahan penjerap yang berbeza. Penggunaan penjerap kos rendah telah disiasat sebagai penyelesaian untuk menggantikan kaedah mahal untuk penjerapan logam berat. Objektif kajian ini adalah untuk menyiasat potensi sisa kulit "rock melon" sebagai penjerap alternatif untuk menjerap Cd (II), Ni (II) dan Cu (II) ion pada larutan akueus. Dalam kajian ini, "rock melon" digunakan untuk menggantikan bahan penjerap yang berkos tinggi yang digunakan dalam industri untuk merawat air kumbahan. Kulit "rock melon" akan dikeringkan ditapis untuk mendapatkan saiz yang sama. Kemudian, serbuk kulit "rock melon" diaktifkan dalam relau pada suhu 400-650˚ C. Penjerapan logam berat dikaji dengan memanipulasi parameter pH larutan, masa sentuhan dan dos bahan penjerap. Keputusan telah dianalisis dengan menggunakan spektroskopi penyerapan atom (AAS). Keadaan proses yang optimum digunakan untuk keseimbangan dan kinetik penjerapan. Penyingkiran peratusan Cd (II), Ni (II) dan Cu (II) telah diukur dan dimodelkan. Peratus penjerapan Cd (II), Ni (II) dan Cu (II) meningkat dengan peningkatan pH, masa sentuhan dan dos bahan penjerap. Walau bagaimanapun, ia cenderung untuk mencapai keadaan keseimbangan apabila bahagian aktif bahan penjerap dihuni sepenuhnya. Keadaan di mana ia memberikan peratus penyingkiran tertinggi adalah pada 120 minit masa sentuhan, pada pH = 8 dan penjerap dos 0.3g yang melebihi 99%. Penjerapan Cd (II), Ni (II) dan Cu (II) ion dari larutan akueus membuktikan pseudo kedua berhasil dengan nilai R2 ialah 1.00 dan k nilai 0,0781-0,1776.

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LIST OF ABBREVIATIONS

AAS	Atomic Adsorption Spectrometer
Ag (II)	Silver (II)
Cd (II)	Cadmium (II)
Cu (II)	Copper (II)
g	grams
HCl	Hydrochloric Acid
L	liter
min	minutes
ml	milliliter
NaOH	Sodium Hydroxide
ppm	Part per million, mg/L
rpm	Rotation per minute
RMS	Rock melon shell
t	Time

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LIST OF SYMBOLS

^oC	Degree celcius
C_e	Equilibrium concentration
C_o	Initial concentration
K_f	Freundlich constant
K_L	Langmuir constant
K_{1ads}	Rate constant of pseudo-first order
K_{2ads}	Rate constant of pseudo-second order
M1	Molarity
n	Heterogeneity factor
q_e	Amount of metal reduction over specific amount of adsorbent
q_m	Maximum adsorption capacity
q_t	Amount of adsorption at time
R^2	Correlation coefficients
V1	Volume

1 INTRODUCTION

1.1 Introduction

In current situation, there are many people concern on heavy metals content that are contaminating our wastewater. It occurs, due to the discharge of large amount of metal contaminated wastewater that is normally from industries, commercial and domestic area. Generally, the wastewater that are generated from industrial were consist of several types of heavy metals such as Cadmium, Nickel, Copper Lead, Zinc and Chromium that are most hazardous among the chemical-intensive industries. It is due to their high solubility in aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorder.

Heavy metals removal from inorganic effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange and electrochemical removal. These processes have significant disadvantages, which are for instance incomplete removal, high-energy requirements and production of toxic sludge (H.Eccleas, 1999).

Adsorption has become one of the alternative treatments, in recent years, the search for low cost adsorbents that have metal bindings capacities has intensified (W.C. Leung et al, 2000). The adsorbents may be of mineral, organic or biological origin, zeolites, industrial by-products, agricultural wastes, biomass and polymeric materials (T.A. Kurniawan et al, 2005). There are many treatment processes that can be used for the removal of metal ions from wastewater, and certainly the cost plays an important role if not crucial the role for determining which one is to be applied. Consequently, in the last few decades alternative sorbents for the treatment of heavy metals contamination have been investigated. The most popular adsorbents among them are microbial biomass and lignocelluloses materials. These are natural materials available in large quantities and being waste products and have a low price.

1.2 Motivation

This work is conducted to remove heavy metal ions including Cd (II), Ni (II) and Cu (II) which has become a global concern in terms of environmental and wastewater aspects. Adsorption is a process one or more component of liquid stream adsorbed on the surface of solid adsorbent and separation is accomplished (Geankoplis, 2003). In this study, rock melon shell acts as adsorbents while the heavy metals are the adsorbate (adsorbed material). Conventional physico-chemical methods for removing heavy metals from waste streams have significant disadvantages and quite expensive and ineffective. Biosorption or biological method has proven to be an effective technology for the removal of heavy metals. Many low cost adsorbent have been used such as carrot residue (Al-Asheh et al. 2002), rice husk (Ghorbani et al. 2012) and tea industry waste (Cay et al. 2004) and for this work rock melon shell will be used as another waste material for the adsorbent.

Conventional treatment technologies for the removal of these toxic heavy metals are not economical and further generate huge quantity of toxic chemical sludge. Cellulosic agricultural waste materials are an abundant source for significant metal biosorption. The functional groups present in agricultural waste biomass viz. acetamido, alcoholic, carbonyl, phenolic, amido, amino, sulphydryl groups etc. have affinity for heavy metal ions to form metal complexes or chelates. The mechanism of biosorption process includes chemisorption, complexation, adsorption on surface, diffusion through pores and ion exchange etc (Sud et al, 2008). In the other hand, rock melon shell could be good adsorbents for the removal of heavy metals instead of being an agricultural waste that may increase environmental pollution in Malaysia. Besides that, this research also aims to convert waste to wealth

1.3 Problem Statement

Increasing in industrial activity is the main point behind most environmental pollution problems and ecosystem damage, coming from the accumulation of pollutants such as toxic metals such as copper, cadmium, nickel, etc (Pino et al., 2006). Heavy metal pollution has become a more serious environmental problem in the last several decades as a result of its toxicity and insusceptibility to the environment. Heavy metals can accumulate in the environment and cause serious damages to ecosystems and human health. Commercial activated carbon has been studied as an adsorbent for removal of heavy metals ions for several years due to the great specific surface area and pore structure, but it is expensive (Depci et al. 2009). Thus, an unconventional of low cost adsorption system is investigate using rock melon shell (RMS) that shows good precursor for activated carbon and was an attractive source in producing high capacity activated carbon.

Besides that, Malaysia Government is working to expand the rock melon farm because of the increasing in demand from the inside and outside of the country. Rock melon was chosen in this project because of its short maturity period of about 75 to 80 days and the huge demand for the fruit overseas. This shell of rock melon is said to be one of many agricultural waste and food industry waste which can cause environmental problem if not treated.

The purpose of this work is to evaluate the adsorption performance of locally derived rock melon shell for the removal of Cd (II), Ni (II) and Cu (II) ions from aqueous solutions by applying the deviation of certain parameters. This work focus on its adsorption kinetic data and the best fits equilibrium adsorption data using Isotherm Langmuir

1.5 Objectives

The following are the objectives of this research:

- To use activated rock melon shell as adsorbent, kinetic and adsorption isotherm of Cadmium (II), Nickel (II) and Copper (II) in aqueous solution.

1.6 Scope of This Research

The following are the scope of this research:

i) This study was done to observe the reduction of Cadmium (II), Copper (II) and Nickel (II) from aqueous solution using rock melon shell waste as adsorbent. The reduction of Cadmium (II), Copper (II) and Nickel (II) from aqueous solution was observed in term of its removal efficiency using the optimum operating condition determined.

ii) Observation and investigation of the effect of process condition for Cadmium (II), Nickel (II) and Copper (II) that can be removed by rock melon shell. During the experiment, the parameters were observed and the equilibrium point for each parameter is used for further investigation.

iii) Determination Cadmium (II), Nickel (II) and Copper (II) removal efficiency by analyzing the result of initial and final concentration for each manipulated variable using Atomic Absorption Spectrophotometer. The manipulated variables for this study are solution pH (pH 2, 4, 6, 8 and 10), contact time (40, 60, 80, 100, and 120 minutes), dosage of adsorbent (0.06, 0.12, 0.18, 0.24 and 0.30 grams) and initial concentration of adsorbate solution (20, 40, 60, 80 and 100 ppm).

iv) Determination of Langmuir adsorption isotherm and kinetic for Cadmium (II), Nickel (II) and Copper (II) that can be removed using rock melon shell as low cost adsorbents.

2 LITERATURE REVIEW

2.1 *Heavy Metals in Wastewater*

Nowadays, heavy metal contaminants in industrial wastewater commonly in petroleum refining, mining activities, paint industry, pesticides and many more have become an anxiety environment issues al all over the world (Ngah, 2008). Commonly there are several metals that have been classified as toxic metals if they are emitted to the environment in quantities that pose risks which including Cadmium (Cd), Nickel (Ni), Copper (Cu), Zinc (Zn), Lead (Pb) and many more (Barakat, 2011; Johnson; Wan Ngah, 2008). Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. So, this can bring serious health effect to human body. Besides that, the exposure of the heavy metals can also defect flora and fauna especially in Malaysia.

Although, heavy metals have many applications to domestic use but the release of these metal may effects human health together with ecosystems (Ozsoy, 2008; Fu, 2011). Nickel (Ni) is one of trace metal essentially need by human especially in stainless steel, catalyst and coins production. However, the excessive level of nickel may cause skin allergic, ingestion problem, asthma, carcinogenesis, causes of cancer and induced lipid peroxidation or cell death (Cempel and Nikel, 2006). Cadmium is not an essential to human life. A study by Bernard (2008) investigate that cadmium is well retained in human body as it was absorbed. Thus, it may cause damage to kidney especially proximal tubular cells as well as bone demineralization and increase the risk of lung cancer. Copper is a chemical element or soft metal with good conductivity. Instead of cadmium, copper also accumulate in human body. It may cause gastrointestinal disturbance, irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Besides, copper also will cause damage to kidney, lung and eyes.

The conventional processes for removing heavy metals from wastewater include many processes such as chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition (Barakat, 2011). However these conventional techniques have their own inherent limitations such as less efficiency, sensitive operating conditions, production of secondary sludge and further the disposal is a costly affair (Ahluwalia and Goyal, 2005a).

Table 2-1: Current treatment technologies for heavy metals removal involving physical and/or chemical processes (Ahmaruzzaman, 2009)

Physical and/or chemical methods	Advantages	Disadvantages
Oxidation	Rapid process for toxic pollutants removal	High energy costs and formation of by-products
Ion exchange	Good removal of a wide range of heavy metals	Absorbent requires regeneration or disposal
Membrane filtration technologies	Good removal of heavy metals	Concentrated sludge production, expensive
Adsorption	flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants	Adsorbents requires regeneration
Coagulation/ flocculation	Economically feasible	High sludge production and formation of large particles
Electrochemical Treatment	Rapid process and effective for certain metal ions	High energy costs and formation of by-products
Biological treatment	Feasible in removing some metals	Technology yet to be established and commercialized

2.2 Activated Carbon As Adsorbent

Activated carbon is coal-based adsorbent that is widely used in industry to remove heavy metal from wastewater (Fu and Wang, 2011). Even though the use of activated carbon is efficient and well establish but it was expensive compared to other adsorbents, so, many researchers investigated a way to reduce the cost of activated carbon by add additives to the activated carbon such as alginate, tannic acid, magnesium and many more. Activated carbon has excellent adsorption properties which have been characterized by high specific area (Lo, et al, 2011). In spite of that, activated carbons have been use extremely because of its ability to removed variety types and amounts of heavy metals. Activated carbon is confirmed to be more efficient in term heavy metal removal but less efficient in term of cost consumption compare to agriculture waste adsorbents.

2.3 Agriculture Waste As Adsorbent

The use of activated carbon will cost a much compare to other adsorbents. Thus, researchers keep a research on searching appropriate adsorbents which using agriculture waste as adsorbents. Biosorption is emerging as a potential alternative to the existing conventional technologies for the removal and/or recovery of metal ions from aqueous solutions. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency, minimization of chemical or biological sludge, regeneration of biosorbents and possibility of metal recovery. Cellulosic agricultural waste materials are an abundant source for significant metal biosorption (Sud et al., 2007). New resources such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk can be used as an adsorbent for heavy metal uptake after chemical modification or conversion by heating into activated carbon (Barakat, 2011).

3 MATERIALS AND METHODS

3.1 *Materials*

i. Rock Melon Shell (RMS)

ii. Cadmium (II) Sulfate

iii. Nickel (II) Sulphate

iv. Copper (II) Sulphate

v. 0.1N NaOH

vi. 0.1N HCl

vii. Nitrogen gas

3.2 *Apparatus*

i. 250ml beaker

ii. 100ml conical flask

iii. 1L and 250ml Volumetric flask

iv. Stopper for conical flask

v. pH meter

vi. Atomic Absorption Spectrophotometer

vii. Glass rod

viii. Dropper

ix. Funnel

x. Whatman Filter paper 125mm

xi. Aluminium foil

xii. Cotton wool

xiii. Gauze cloth

3.3 *Overall Methodology Flowchart*

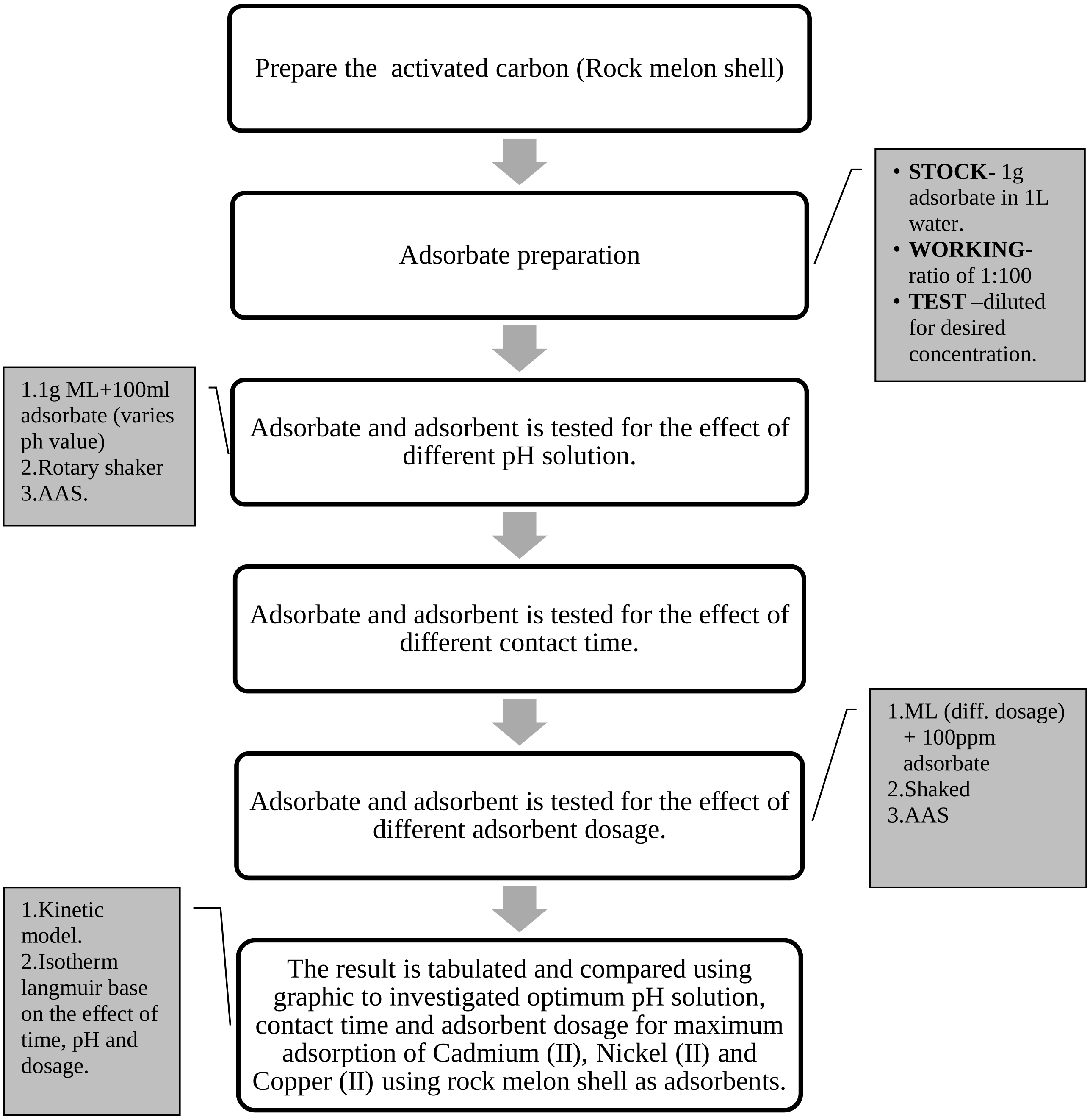

Figure 3-1: Overall flow chart for experimental methodology.

3.4 Experimental Methodology

3.4.1 Activated Carbon Preparation (Rock melon shell)

Rock melon shell (RMS) waste will be used as the main raw material in this work. The RMS will be dried crushed in a mill to get a grain size of 2mm. Phosphoric acid 40 % w/w will be added to the crushed shells at a ratio of 1:2 (g GAC/g H3PO4) to prepare the impregnate samples. These samples will be carbonized in a furnace at 500–700˚C for 1.12 h under nitrogen (N2) flow of 120 mL min-1 at a heating rate of 10 ˚C min-1. The carbonized sample (activated carbon) will be washed several times with distilled water to remove the phosphoric acid, and then check the pH of the washing water until the value is constant. Then the activated carbons will be dried in an oven at 80 ˚C per 24h.

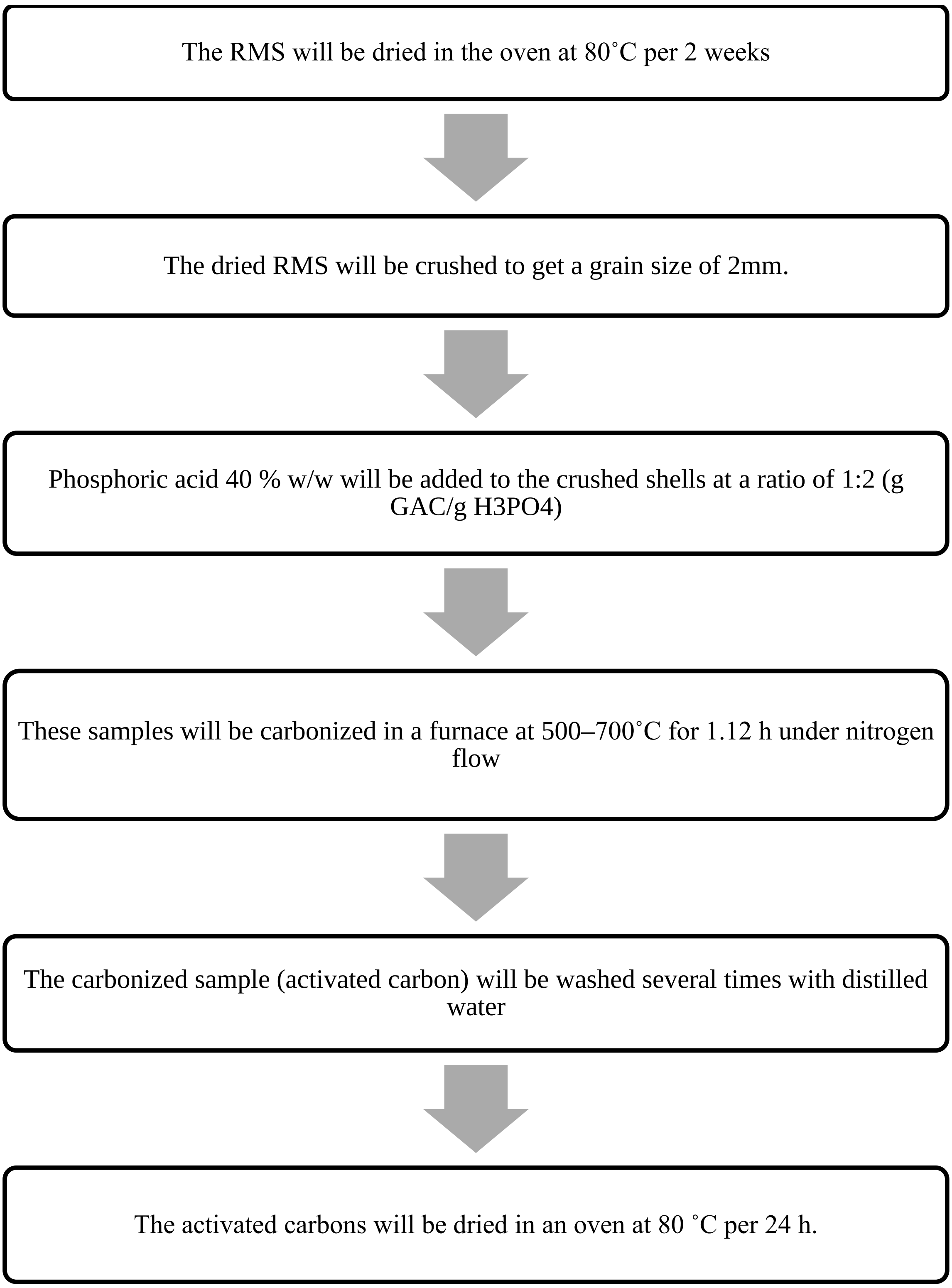

Figure 3-2: Flow diagram of preparation of rock melon shell (RMS)

3.4.2 *Adsorbate preparation*

This work will be conducted based on three heavy metal which are cadmium (II), nickel (II) and copper (II). Stock solution will be prepared by dissolving 100mg of cadmium (II) sulphate, nickel (II) sulphate and copper (II) sulphate in 1L of distilled water in different volumetric flask.

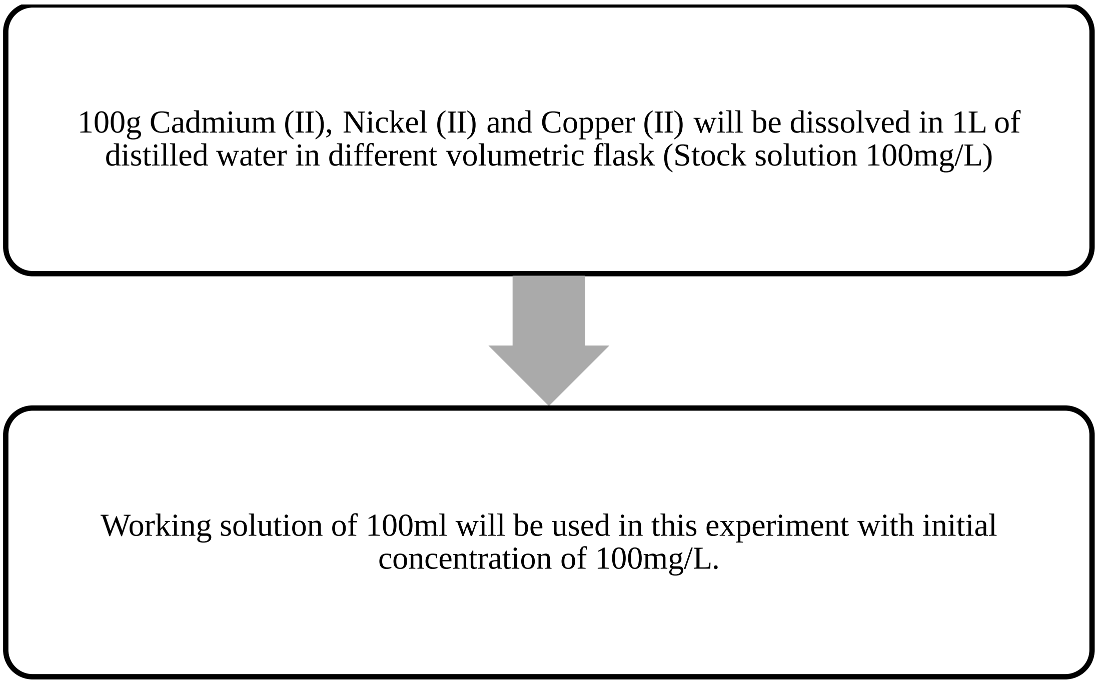

Figure 3-3: Flow diagram of preparation of adsorbate

3.4.3 *Effect of pH*

This experiment involve adsorption process which the RMS powder is use as adsorbents. 0.3 g of the adsorbent kept constant with 100 ml adsorbate for this experiment. 0.1N NaOH and 0.1N HCl is used to change pH from 2 to 10 so that the change in volume of the solution can be negligible. Adsorbate solution will be performed at 25˚C at the variable pH value which are 2, 4, 6, 8 and 10 on a rotary shaker operated at 150 rpm for 2 hours. The sample is filtered using Whatman filter paper 125mm before analyzed with Atomic Adsorption Spectrometry.

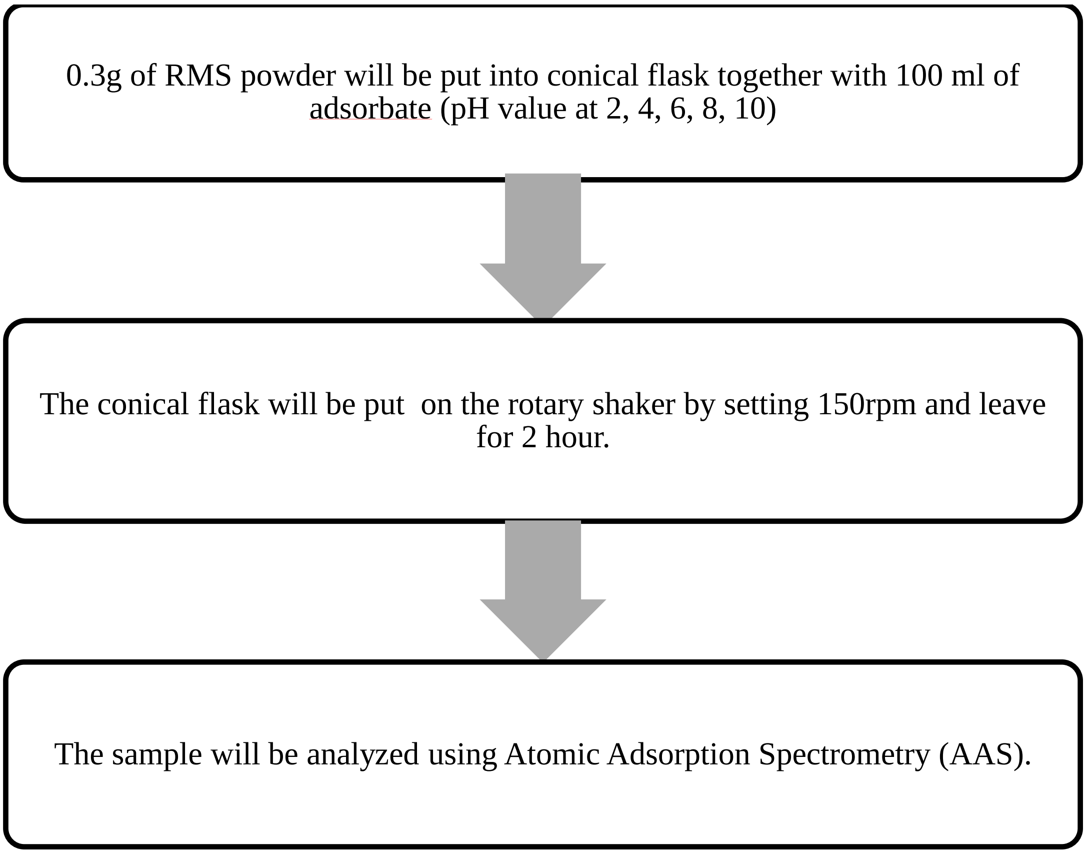

Figure 3-4: Flow diagram of the effect of initial adsorbate solution concentration (pH solution)

3.4.4 *Effect of Contact Time*

In order to evaluate the effect of contact time over heavy metals removal, the adsorbate solution is mix with 0.3g of rock melon shell powder. The mixture then shake on a rotary shaker operated at 150 rpm and 25˚C. The effect of contact time is investigated with varies of time which was 20 minutes to 2 hours with the gap of 20 minutes at optimum pH from previous experiment. The sample is filtered using Whatman filter paper 125mm and analyzed with Atomic Adsorption Spectrometry.

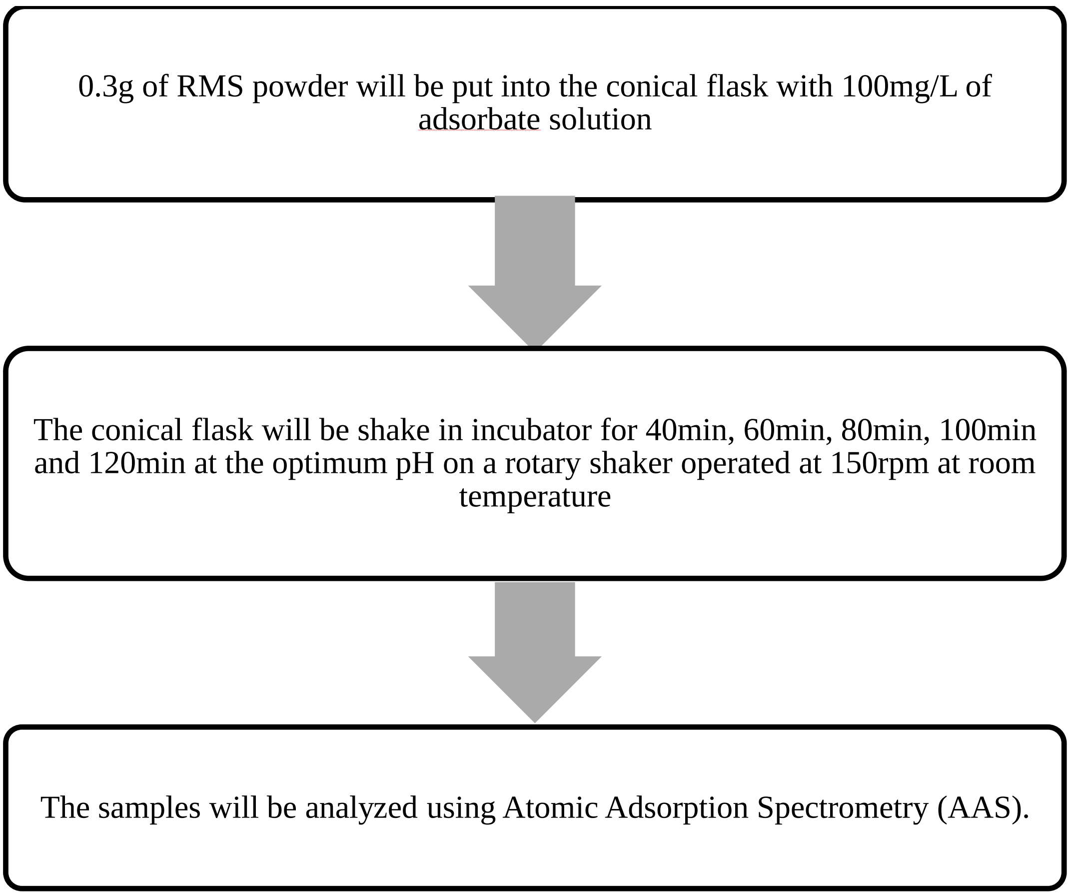

Figure 3-5: Flow diagram of the effect of contact time